

COLLOIDAL FERRIC HYDROXIDE AS
A CAUSE OF THE BOND IN
MOLDING SANDS

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COLLOIDAL FERRIC HYDRATE IN MOLDING SAND ¹

The Influence of a Surface Film of Hydrated Iron Oxide on the Bond in Sand-Clay-Water Systems.

BY CLYDE C. DEWITT AND GEORGE GRANGER BROWN

1. INTRODUCTION

The production of cast metal articles has always been one of the fundamental industries. During the last decade the increase in the manufacture of castings, both ferrous and non-ferrous, has been so great as to threaten the exhaustion of natural deposits of molding sand which are necessary to the production of good metal castings.

A molding sand has been defined by Littlefield ² as any material which when moist can be formed into a mold from which usable metal castings may be made. This definition includes all combinations of sand and clay or other material, and it implies all desirable qualities that a molding sand must have, the two most important of which are bond, so that the mold may have sufficient strength to support the metal while being poured, and permeability to gases, so that the gases may readily escape giving a sound casting free from blow holes.

The cause of permeability is reasonably well understood and satisfactory tests for this property have been developed, adopted and are in constant use.

Of the cause of bond in molding sand very little definite information is available. It has been thought that the presence of iron oxide had something to do with the bond,³ but there is also some evidence that is contradictory.⁴ Little agreement is found concerning the origin and condition of the iron oxide even among those who consider iron oxide important in giving bond to a sand.

Condit ⁴ states that the hydrated iron oxide films on sand and clay particles are formed by precipitation of iron salts from surface water. "Surface waters charged with organic acids readily dissolve iron. As these waters percolate downward the iron is precipitated between the

¹ Part of a dissertation submitted in partial fulfillment of the requirements for the degree of Doctor of Philosophy in the University of Michigan by C. C. DeWitt.

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² Littlefield, *Ill. State Geol. Survey*, Bull. No. 50, 1925, p. 20.

³ King and Schlichter, *U. S. Geol. Survey*, 19th Annual Report (1899); Boswell, *Engineering*, 108, 418-20; 464-66 (1916); *Foundry*, 47, 593 (1919); *Trans. Am. Foundrymen's Assoc.*, 27, 305 (1918); Hanley and Simonds, *Foundry*, 48, 772-4 (1920).

⁴ Condit, *Trans. Am. Foundrymen's Assoc.*, 21, 21-27 (1912); Moldenke, "Principles of Iron Founding," McGraw-Hill Book Co., N. Y., 1917.

sand grains. For this reason the grains of most molding sands are thickly coated with limonite."

In direct contrast to Condit's views, Gordon⁵ accounts for the presence of colloidal gel coatings on silicate particles as formed by decomposition of the sand grains themselves. Whitney⁶ also considers that the soil colloids are derived from the sand particles which become hydrolyzed not by being precipitated from solution but by molecules of water bombarding the soil particles when they have reached a diameter of 0.0001 mm.

Boswell⁷ reports the beneficial effects of iron oxide as a binder in the British red sands as follows:

"The chief natural bonds in molding sands are ferric hydroxide and clay substance (silicate of alumina, fine micas, etc.). These like many of the artificial bonds in common use, are colloidal bodies. The adsorptive power of clay, in the matter of both gases and solutions increases, according to Senfft, with the limonitic content. J. Van Bemelen found as long ago as 1878 that the amount of 'hydrate water' of ferric oxide was variable and accidental. When just dry at 15° C. the compound is able to take up over six molecules of water per molecule of ferric oxide. One of the most marked characteristics of the best sands is their extraordinary power of taking up considerable quantities of water without really becoming wet. The following figures, for example, are those of hygroscopic water (liberated at 110° C.) contained in molding sands (some of them moist but none wet) as collected in the field.

	Per cent
Cornish Red	11.6
Erith stone	10.2
Belgian Yellow	6.6 partly dried
Wolverhampton	13.5
Kiddermaster	8.0

"Another important desideratum of good molding sands, possibly connected with the colloidal character of the bond, is that they should not 'go dead,' that is, dehydrate too readily after metal has been cast in them. Iron oxide readily hydrates again, unlike clay which may be 'porcelainized' by heat.

"The distribution of the bond in naturally bonded sands is ideal. Each grain of quartz is coated with a thin pellicle of ferric hydroxide or ferruginous clay. Water skins cannot hold on to clean quartz, but each coated grain assumes the skin of water, which with its neighbors constitutes the enormously strong 'green bond' of the sand.

"It is noteworthy that in the West European sand the higher the percentage of ferric hydroxide the greater is the transverse strength in the sands. In the case of the sand from south Africa containing 4.81

⁵ Colloid Symposium Monograph. Vol. 3, p. 114 (1924).

⁶ *Science*, 54 656 (1921).

⁷ *Engineering*, 108, 418-20, 464-66 (1916).

per cent of ferric hydroxide, the molds produced were of extraordinary strength and toughness."

Hanley and Simonds⁸ express their belief that the majority of the well bonded molding sands of this country owe their bonding qualities to the presence of colloidal hydrated ferric oxide as follows:

"In the study of many sands surprising results are obtained in connection with the effect of iron oxide on the bonding property. . . . Just what composes the 'clay substance' (bond) in molding sand is not generally understood, and the following analyses of the bonding material after it is separated from the sand may serve to clear up this point.

	New Jersey Sand	Ohio Sand	New York Sand
	Per cent	Per cent	Per cent
Silica	41.70	33.65	38.88
Iron Oxide	14.27	28.88	24.67
Alumina	25.40	18.15	22.50

In another article Hanley and Simonds⁹ state, "Ferric Oxide practically always is present as an impurity in natural molding sands, and its percentages as shown by chemical analyses, often give a good indication of the amount of the bond in the sand. Ordinarily common sand without bonding properties will show an iron oxide content of 5 to 6 per cent, whereas in molding sand the ferric oxide may run from 3½ to 15 per cent. The importance of the iron content of a sand is not generally recognized, but from experience with a large number of sands with varying iron content, it has been proven that a relation exists between the percentage of iron oxide and the bonding quality. The iron content alone is not sufficient in some cases, for a sand containing five or six per cent may have almost no bonding property or it may have a fairly good bond."

Bean¹⁰ considers iron oxide detrimental in molding sand even when present in small amounts. His views are criticized by Shaw.¹¹

Moldenke¹² considers iron oxide bad, but admits to a limited degree its beneficial action on bond as follows:

"A further noticeable point in a number of so called 'red' sands is a very high percentage of iron oxide, this rising to 7.5 per cent in some English sands. In one case near Vienna a sand is used with over 11 per cent iron oxide, and again another sand with nearly 12 per cent of lime. Both of these ingredients are bad, as they are fluxing, but it is interesting to note that a moderate percentage of iron oxide, if distributed over the surfaces of the quartz crystals as a stain and encrustation is not objectionable to a serious extent, as it serves as a base to hold the clay more firmly to the otherwise smooth surfaces of the grains, particularly if they are well rounded."

⁸ *Foundry*, 48, 722-4 (1920).

⁹ *Foundry*, 48, 743 (1920).

¹⁰ *Trans. Am. Foundrymen's Assoc.*, 26, 419 (1917).

¹¹ *Trans. Eng. Ceram. Soc.*, 13 (1913-14).

¹² "Principles of Iron Founding," McGraw-Hill, N. Y., 1917.

Boswell¹³ notes that molding sands fall into two classes, naturally bonded sands which contain ferric hydroxide or certain silicates, and high silica sands which must be bonded artificially with such substances as sugar, dextrin, molasses, oil, or sulfite lees. He¹⁴ states that the ferruginous bond improves the life of the sand and assists in the production of a smooth sound surface to the casting particularly in the case of steel. It should be noted that this view is practically the opposite of that held by Moldenke and Bean.

Kennedy¹⁵ calls attention to the fact that all attempts to produce artificial molding sands with the same bond as natural sand have been unsuccessful because of improper distribution of clay around the grains, giving a sand lacking in durability. He suggests that these failures are due to a lack of knowledge of the properties of iron oxide as a binder, and of ability to coat sand grains with colloidal hydrated iron oxide. Although it has been recognized for some time that colloidal ferric oxide films might have an important influence on the bond strength of sands, no quantitative data have been presented to show the effect of such films, or to account for the bond in molding sand in terms of such films.

This paper reports quantitative data showing the relation of colloidal ferric oxide adsorbed on the sand grains and on the clay bonding material to the strength of bond in the molding sand, and the successful preparation of synthetic molding sand obtained in the course of work done on Michigan sands for the Michigan Geological Survey. The effect of colloidal iron oxide on the bond of molding sands has been determined by analytical methods on natural sands; and by synthetic methods successfully reproducing the bond of natural molding sand by the proper combination of clean unbonded sand or silica, kaolin, and ferric hydrosol.

2. TESTING METHODS

Five four-hundred-gram portions of the dried sand were weighed out and each mixed in either a tin or an aluminum dish with enough distilled water measured from a burette so that the samples would contain approximately 4, 6, 8, 10, 12 per cent of water respectively. In some cases when only four samples were taken, the same range of percentage water content was covered at slightly different intervals. As soon as the samples were mixed they were put into clean Mason jars provided with rubbers and sealed. The samples were allowed to stand for at least twenty-four hours before being tested.

At the end of twenty-four hours the jars were opened and samples prepared for permeability and bond tests.

¹³ *Foundry*, 47, 148-50 (1919).

¹⁴ Boswell, *Jour. Inst. Metals*, 22, 292 (1919).

¹⁵ "A Summary of the Literature on Molding Sand," *Am. Foundrymen's Assoc.*, 1922.

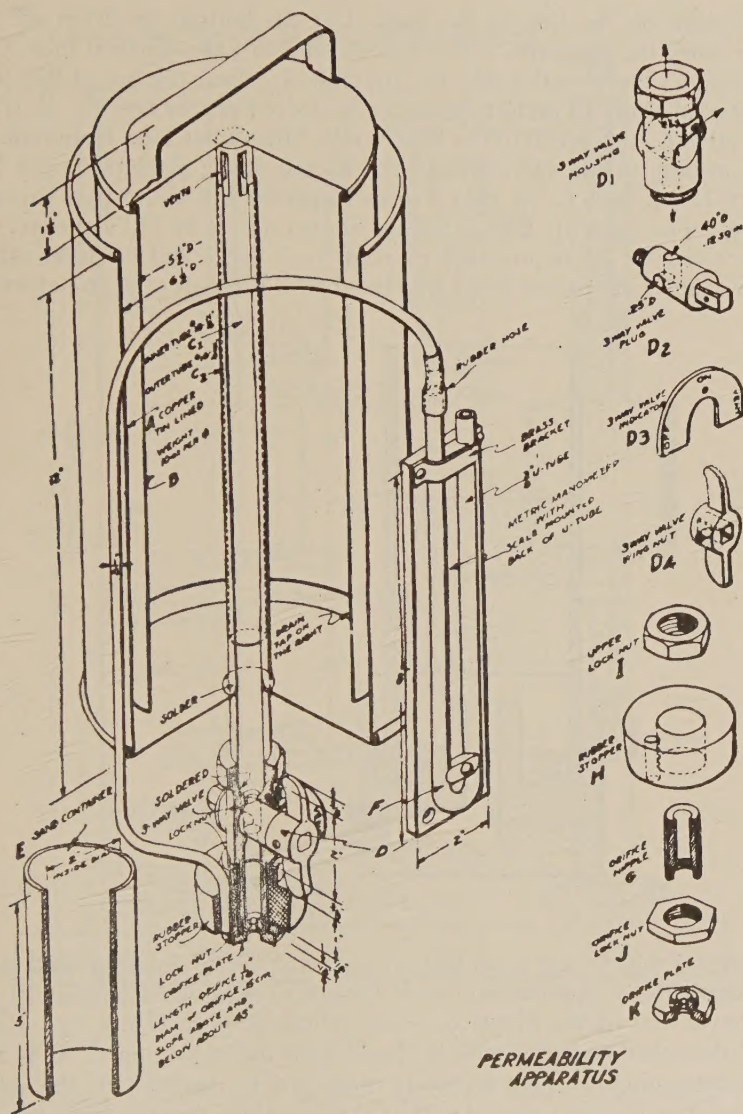


FIG. 1.

Permeability.—The test used for permeability is that adopted by the American Foundrymen's Association. The permeability apparatus¹⁶ is shown in Figure 1. Tank *A* is made of copper, tin lined and is provided with a vertical air outlet tube coming through the bottom of the same. When in use this tank is partly filled with water. A stopcock

¹⁸ *Trans. Am. Foundrymen's Assoc.*; Vol. 31, pp. 708-721.

is provided on the side of the tank *A* at the bottom, to drain off the water when the apparatus is not in use. Bell *B* has a vertical tube, *C-1*, which slides inside outlet tube *C-2*, in tank *A*. Near the top of this tube are several vents to permit the air to be forced out of bell *B*. A three way valve *D* is attached to the lower end of the outlet tube from tank *A*. The opening in the valve should not be too small, preferably not less than 0.12 sq. inch (3 sq. mm.) so as to permit the air to pass through freely. The parts of this valve are shown as *D*₁ to *D*₄ inclusive. A valve indicator, *D*₃, is provided, marked "on," "off," and "vent," to show when valve is in position to let air from bell *B* through sand container *E*;

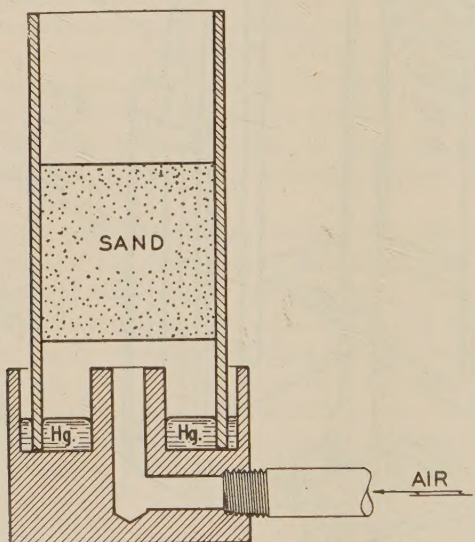


FIG. 2.

to shut off flow of air from bell, or to permit air to enter by pass while raising the bell. An orifice plate *K* for use in rapid work is screwed into the lower end of the nipple *G*. The rubber stopper *H* fits into a steel shell the other end of which is closed with the exception of a $\frac{1}{8}$ inch projecting nipple. This nipple is connected to the inlet of the device for holding the compressed sand cylinder while the air from the bell is passing through it.

The device shown in Figure 2, used to hold the cylinder containing the sample of sand while the permeability test is being made, is a block of cast iron in which an annular groove 1 inch inside diameter, 3 inches outside diameter, $1\frac{1}{2}$ inches deep is cut. The hub of the annular groove is drilled centrally to within half an inch of the bottom of the piece. At an elevation of one side of the piece sufficient to leave a small portion

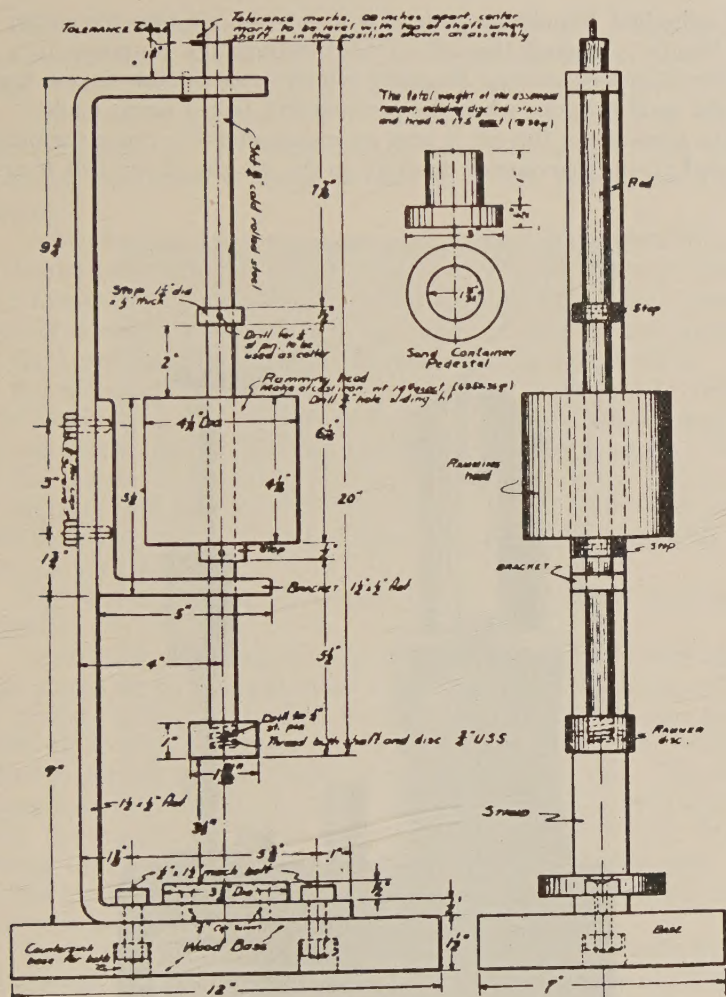


FIG. 3.

of the centrally drilled hole as well, a hole is drilled and tapped for a $\frac{1}{8}$ inch pipe nipple. A $\frac{1}{8}$ inch nipple screwed tightly into the hole serves as the gas inlet. A short length of heavy walled rubber tube is used to connect this nipple with that on the bottom of the steel shell attached to rubber stopper *H*. A steel cylinder 2 inches internal diameter $2\frac{1}{4}$ inches outside diameter 5 inches long is used to form the sample. The cylinder containing the formed sample is placed end on in the annular groove, which is filled half full with mercury to form a seal that prevents the escape of air coming from the gasometer.

As the bell *B* sinks in tank *A* it drives the air into the outlet pipe *C-I*, Figure 1, through the valve *D* and through the container *E*, a steel cylinder 2 inches internal diameter which is set in the device used to hold the sand cylinder when the permeability test is being made.

The pressure of this air is read on manometer *F*. Since the pressure recorded on the manometer depends on the weight of the bell *B* and on

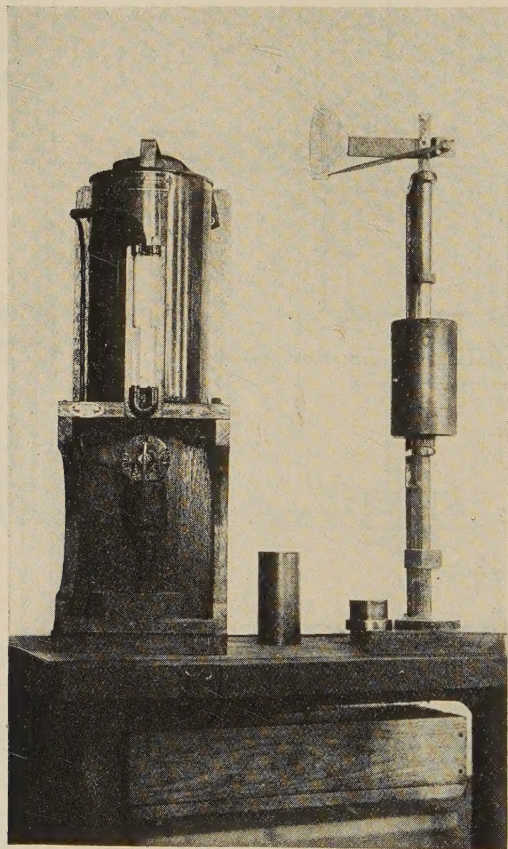


FIG. 4.

its cross sectional area a weight is provided which can be placed on top of *B*, sufficient to increase the manometer pressure readings to 10 centimeters of water.

The detailed drawing of the sand rammer for the permeability test is shown in Figure 3. It consists of a steel rod supported by two guides. A steel disc is attached to the lower end of the rod, and has a sliding

fit in the sand container *E*. A cast iron weight weighing 14 lbs. (6350.36 grams), slides on the rod, its movement being regulated by two stops. The distance between these stops is sufficient to permit a 2 inch movement of the rammer head. A pedestal is provided on which the sand container *E* rests while sand is being placed in it; and while the ramming operation is being performed. The pedestal is shown in Figure 4.

In place of the tolerance gage, used in the A.F.A. apparatus, shown in the drawing at the top of the guide rod frame, an indicator, consisting of a brass frame on which is pivoted a light beam carrying a knife edge contact one inch from one end was used. A stop on the pivoted side of the beam prevents the beam from jumping out of position. A scale at the end of the indicator beam is calibrated between 1.75 inches and 2.25 inches by hundredths of inches by placing Johannsen gage blocks of the proper size on the pedestal underneath the rammer. The face of the rammer is caused to rest on the gage blocks, the indicator beam is swung over so that the knife edge touches the top of the steel guide rod and the point at the tip of the beam marked on the scale with a short line for each .01 inch.

Figure 4 shows the photograph of the permeability apparatus and rammer.

In preparing the specimens, container *E* of the permeability apparatus was placed on its pedestal, filled almost level with the sand and placed in position under the rammer head. The rammer head and guide rod were allowed to rest momentarily on the sand while the weight was lifted to contact with the upper stop and allowed to fall. The ramming operation was repeated a total of three times on each sample, after which with the weight and guide rod in position, the indicating beam was swung over until the knife edge bearing came in contact with the top of the guide rod. Thus the height of the rammed specimen was read and recorded.

Tank *A* of the gasometer was filled with water to within $4\frac{3}{4}$ inches of the top. Valve *D* was opened to "Vent" and bell *B* raised until the zero mark was a little above the top edge of *A*. Valve *D* was turned "off." The sample and its container *E* were placed end on in the device having the annular groove half filled with mercury, and Valve *D* turned "on." The time taken for the bell to sink from the zero mark on the side of the bell to the 2000 mark on the bell was noted by means of a stopwatch, and recorded. The difference in levels of the water manometer *F* was recorded. The permeability of the sand was calculated by the following equation:

$$\text{Permeability} = \frac{(\text{cc. of air}) \times (\text{cm. height of specimen})}{(\text{gms. pressure}) \times (\text{area in sq. cm. of specimen}) \times (\text{time in minutes})}$$

Bond or Strength.—The indication of the bond of molding sand has been accomplished by several methods: by the dye adsorption method and by certain physical tests such as failure of a prepared sample in transverse, tensile, compression, or shear.

For some time it has been recognized that the dye adsorption test as applied to molding sands is not an exact index of the amount or quality of the bonding material. Gordon¹⁷ and his collaborators have shown that for certain types of dyes a true chemical equilibrium exists where certain dyes are used to determine the soil colloids. An unpublished work of Crane¹⁸ confirms this conclusion of Gordon. In general the dye adsorption test is not considered a satisfactory indication of bond strength among foundrymen and scientific investigators such as Moldenke,¹⁹ Hanley and Simonds,²⁰ Doty,²¹ Condit,²² Harrington,²³ Bradfield.²⁴

Considerable difference of opinion is expressed by various investigators on the relative values of the various physical tests in indicating the strength of the bond in molding sand. The difference of opinion seems to be about equal to the number of types of machines brought forth by the sponsors of these tests. Adams²⁵ has made a careful survey of the different types of testing machines that have been described in the literature up to 1926. Inasmuch as the compression test seemed to afford one of the best known tests of bond strength, a machine for testing the bond strength of molding sands by failure in compression was constructed as shown in Figures 5 and 6. The principle upon which the machine is built is that of a simply supported beam, between whose supports a weight is caused to travel at a constant rate.

This testing machine offers the following advantages:

1. No initial loading of sample.
2. Freedom from impact fuses.
3. Constant rate of loading.
4. Automatic operation, stopping and indication of breaking load.
5. Accurate and sensitive to less than one gram.

The rammer used in preparing specimens for compression tests (Figure 7) is somewhat similar to that used in the permeability tests, being an adaptation of that described by Dietert.²⁶ It consists of a steel rod supported by a steel frame. The guides of this steel frame are drilled to give the steel rod a sliding fit. A cast iron head weighing exactly seven pounds slides on the rod. Stops pinned to the steel rod

¹⁷ "Colloid Symposium Monograph," Vol. 2, p. 114 (1924).

¹⁸ Private Communication to the authors through Prof. Chas. H. Behre of Geology Dept. of Univ. of Cincinnati (1926).

¹⁹ *Op. cit.*

²⁰ *Trans. Am. Foundrymen's Assoc.*, 28, 741 (1920); *Foundry*, 48, 772, 867, 921 (1920).

²¹ *Trans. Am. Foundrymen's Assoc.*, 30, 796-822 (1921).

²² *Ibid.*, 21, 19-52 (1913).

²³ Harrington, Wright, Macomb, *ibid.*, 30, 782-796 (1922).

²⁴ *J. Am. Chem. Soc.*, 45, 2669 (1923).

²⁵ *Trans. Am. Foundrymen's Assoc.*, Preprint No. 26-1 (1926).

²⁶ *Trans. Am. Foundrymen's Assoc.*, 33, 721-757 (1925).

sample, the beam of the indicator was swung into position so that the knife edge bearing came in contact with the top of the guide rod and the height of the sample read to the nearest 0.005 inches from the scale and recorded.

The samples were rammed from one end only. The reason for this was to eliminate any possibility of error in preparation, that might be due to any small misalignment of the sand cylinder top and bottom rammer which might occur if the sand were rammed from both ends causing the three to bind and stick or otherwise absorb the kinetic energy which should have gone into compressing the sand sample to the re-

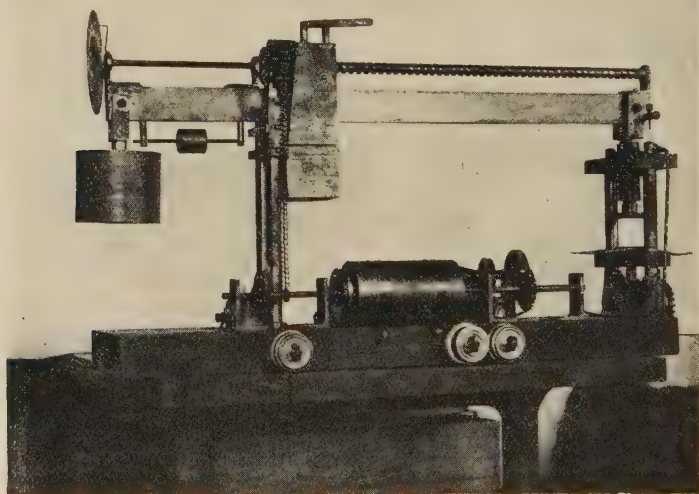


FIG. 6.

quired dimensions. Preliminary work showed this precaution to be a refinement necessary for consistent results. Reversing the ends of the samples rammed from one end only in the testing machine showed no difference in breaking strength.

The samples were stripped from the cylindrical mold by lifting the mold off the pedestal and pressing the sample out of the mold on a long steel pedestal or column of like diameter. The sample was grasped between the thumb and forefingers and the excess sand blown off each end.

The sample was then placed on the movable face plate *F* of the compression machine, Figure 5. The motor having been started and switches (*b*, *c*, *d*, *e*) closed, the position of the sample adjusted to bring it almost into contact with the upper surface *E* by means of the hand wheel

raising and lowering *N*. Switch *d* was snapped off setting the weight in motion. When the sample was broken the weight was automatically stopped indicating the breaking load by its position. The crushing plates were carefully wiped free of sand, and opened by turning the hand wheel. Some broken parts of the sample that fell were caught

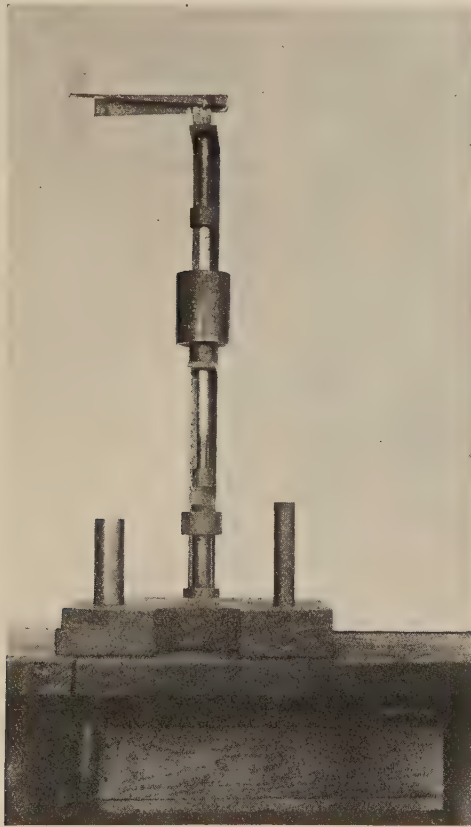


FIG. 7.

on a clean piece of paper placed below the front end of the machine; the sand which came in contact with nothing other than metal or paper or wooden table top was returned to an individual container provided for that particular sand.

The cylindrical mold was carefully cleaned by drawing a clean cloth through it and any sand that might be near the pedestal or on it was removed after each determination. When a completed series of tests

on one sample had been run any scattered sand on the machine and the table where the ramming had been done was carefully brushed up and returned to the container.

At least three and in most cases five or more individual checks were made on each sample. The simple relation suggested by Hansen²⁷ that the breaking strength of a cylindrical sample of constant diameter and constant water content is inversely proportional to its height, can be applied through a narrow range in height as from 1.80 to 2.05 inches with an error of less than 2 per cent in most cases. This allowed the direct computation of the breaking strength to a height of 1.95 inches, the height at which the reported strengths are computed. The method of computation involved the multiplication of each breaking strength by the height of the sample broken, averaging the numbers so obtained and dividing their sum by 1.95. This method made it unnecessary to have all test specimens the same height.

Determination of Water Content.—The water content of the sample of sand contained in each jar was determined on a whole sample of 38-80 grams of sand prepared in the usual manner. The sample was placed in a weighing bottle, weighed, dried for 24 hours at 105-110° C., cooled and reweighed, the difference in weight was regarded as the water content. The water content of sand samples after testing varied slightly, not more than 0.1 per cent, from the moisture content of samples taken from the bottle. The difference was within the experimental error so that it really made little difference whether the sample for moisture content was taken directly from the bottle or from the fragments of a test specimen.

Water Still.—At the outset it was thought desirable to have available large quantities of very pure water to eliminate the uncertainty in colloidal systems for using impure water. A continuous column still of relatively high capacity was designed and built to supply this need. This equipment comprised two still bodies with steam coils, two columns interconnected and two condensers one at the top of each column as shown in Figure 8.

The water is vaporized in the first still body. The vapor travels upward through the packing of the first tower, a portion of it is refluxed down the tower and is discarded through a trap at the bottom, thus effecting a separation of the less volatile impurities. The remainder of the vapor travels across to the second tower where it is condensed, flows down through tower packing, meeting as it comes down an upward current of steam generated from pure distilled water in the second still body, part of which escapes through an orifice in the top of the second tower carrying off the more volatile impurities. At the base of the

²⁷ *Trans. Am. Foundrymen's Assoc.*, **32**, 57-97 (1924).

second tower some of the water is tapped off through a trap, the balance going into the still body to be revaporized to furnish the steam for scrubbing the water coming down the column free of more volatile impurities and gases.

All parts of the still coming in contact with the water or water vapor are made of block tin. The packing in the columns is made of

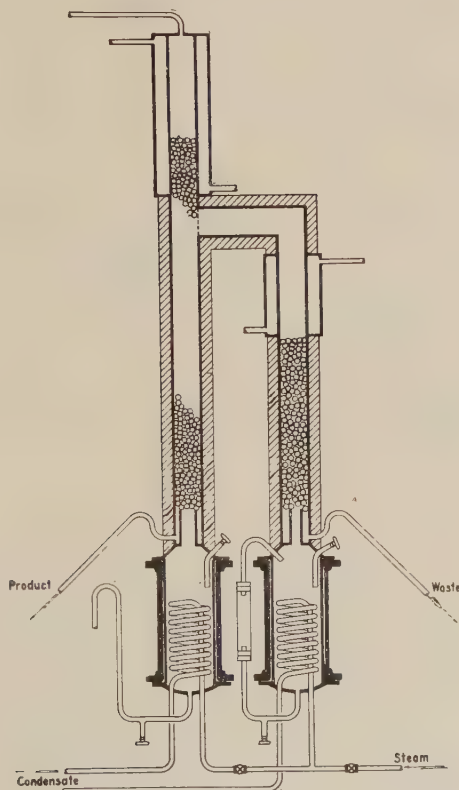


FIG. 8.

one-fortieth inch sheet block tin cut and formed into Raschig rings three-fourths inch diameter by three-fourths inch thick.

3. ANALYSIS OF NATURAL MOLDING SAND

For the purpose of investigating the cause of bond in natural molding sand a sample of fresh Albany molding sand was adopted for testing and analysis. The Albany sand is a more durable sand than can be

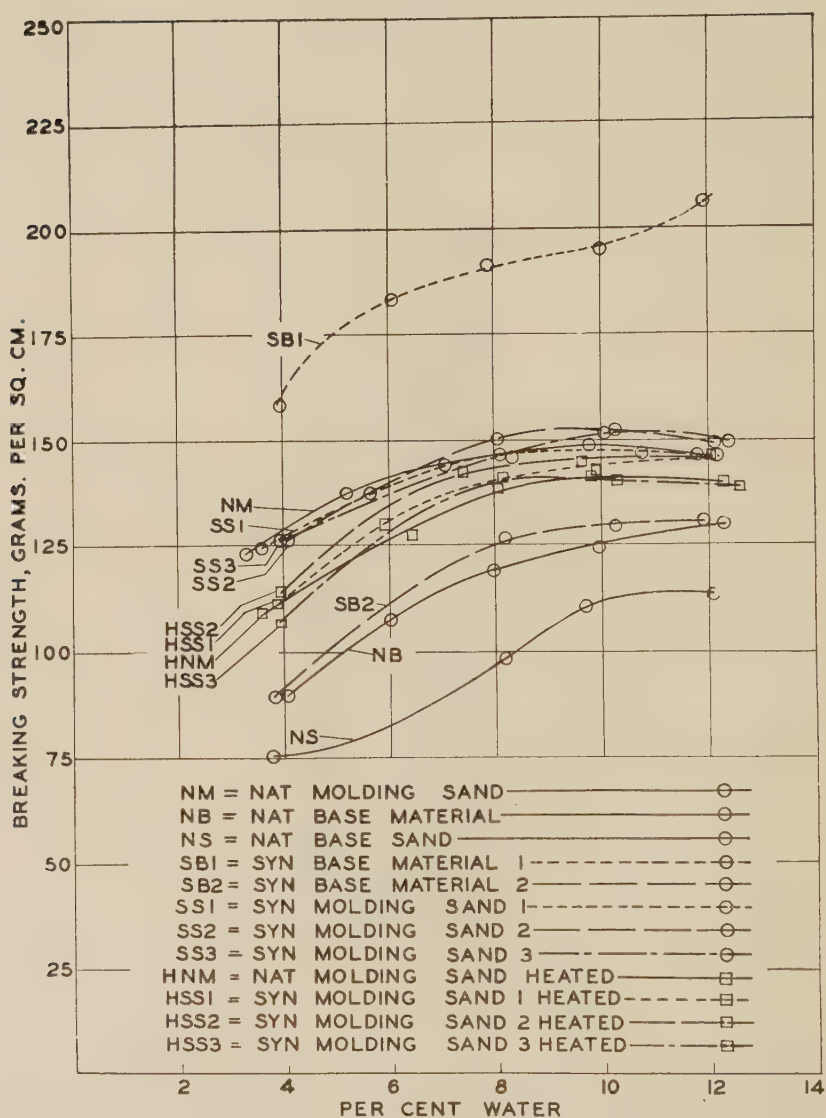


FIG. 9.

obtained in Michigan and is representative of sands containing the most satisfactory bond.

Natural Molding Sand.—The natural Albany molding sand was carefully dried in air, and at 105-110° C., then thoroughly mixed and quartered to yield a sample of 2,000 grams which was preserved in a glass jar.

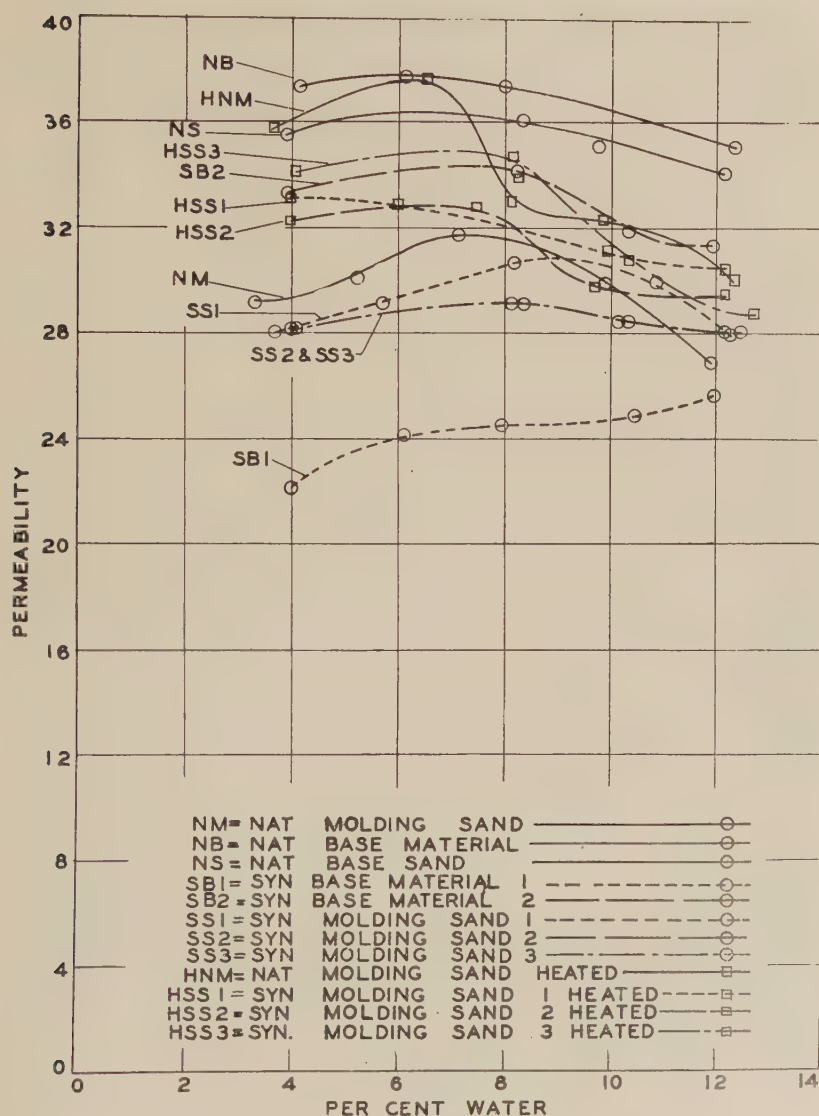


FIG. 10.

This sand was tested for bond and permeability by the methods described and with the results given in Table 1. The compressive strength in grams per square centimeter is plotted as a function of moisture content in Figure 9 and the permeability plotted as a function of moisture content in Figure 10.

TABLE 1.—PROPERTIES OF THE NATURAL MOLDING SAND.

Percentage H ₂ O	Breaking 2/3 Gms. per Sq. In.	Strength in Lbs. per Sq. In.	Compression Gms. per Sq. Cm.	Permeability
3.3	532	1.760	122.9	29.2
5.2	576	1.906	137.6	30.1
7.14	624	2.064	144.15	31.8
9.82	646	2.137	148.2	29.9
11.83	634	2.098	146.4	27.0

Natural Base-Material.—The natural base-material was prepared from the natural molding sand by removing all of the clay silt, or loam surrounding the individual sand grains, which could be removed by washing with water.

The so-called "clay substance" was removed from the natural Albany molding sand by repeated washing and shaking with tepid distilled water. Some 40 lbs. of sand were distributed in clean quart Mason jars one-half pound of sand to each jar. Twenty jars of sand were treated at one time. Each jar of sand was filled with distilled water to about two inches from the top. The jar was tightly stoppered, thoroughly shaken, and allowed to settle until the last one of the jars had been so treated. The water was then siphoned out of the first jar, care being taken to have the end of the three-sixteenths-inch rubber tube siphon at least three-fourths inch above the level of the sand layer that had settled out. The water suspension of silt, etc., siphoned off was caught in an enameled pan and transferred to a steam jacketed Duriron kettle. This operation was repeated on each of the jars continuously for about two weeks, at the end of which time the water above the sand could be seen to be perfectly clear. In the meanwhile all the washings and silt had been evaporated to dryness, collected and weighed. It constituted about 13 per cent of the original dried sample. A screen analysis indicated that all of this material passed through a 270-mesh sieve.

The natural *base-material* of the molding sand was washed out of the jars into an enameled container, excess water decanted through a filter paper on a Buchner funnel, the sand so caught returned to the container. The natural base-material was air dried, then dried for one hour at 105° C. and mixed for testing.

SCREEN ANALYSIS.

Mesh	Per cent on
50.....	0.028
60.....	0.268
70.....	0.422
80.....	0.235
100.....	0.622
140.....	20.582
200.....	40.600
270.....	25.950
Pan.....	11.990

The screen analysis of the natural base-material was made by sifting for 30 minutes 100 grams of the material obtained by quartering in the usual manner, using U.S.S. screens and a Rotap machine.

The base-material was tested for bond and permeability by the methods described and with the results given in Table 2. The compressive strength in grams per square centimeter is plotted as a function of moisture content in Figure 9, and the permeability in Figure 10.

TABLE 2.—PROPERTIES OF THE NATURAL BASE-MATERIAL.

Percentage H ₂ O	Breaking Strength in Compression			Permeability
	2/3 Gms. per Sq. In.	Lbs. per Sq. In.	Gms. per Sq. Cm.	
4.11	385	1.274	88.9	37.3
6.03	465	1.538	107.5	37.3
7.97	515	1.704	119.0	37.5
9.97	539	1.782	124.5	36.4
12.28	564	1.865	130.25	35.2

The Natural Base-Sand.—The natural base-sand was prepared by removing the adsorbed material from the natural base-material. A large portion of the natural base-material was treated with 1 per cent caustic soda solution and shaken, then washed with water, and digested with hot 1-1 HCl to dissolve any film of hydrated oxides. The sand was washed repeatedly by decantation alternately at first with hot dilute acid and hot distilled water, finally with hot distilled water until the washings were free from acid. The sand after this treatment is hereafter referred to as the natural base-sand. This material was kept under distilled water which was changed frequently until no more acid, as determined by the colorimetric hydrogen-ion method diffused into the water. The base-sand was then collected and dried at 110° C. Its general appearance had changed from dull greenish brown to a light gray shot with sparkling bits of mica.

The iron oxide removed from the base-material by hot 1-1 HCl was determined and found to be 2.6 per cent. The total weight of ignited oxides removed by hot 1-1 HCl was 0.0272 grams per gram of sample or 2.72 per cent. This analysis indicated that practically all of the material removed by the HCl was iron of one form or another.

The natural base-sand was tested for bond and permeability by the methods described with the results given in Table 3. The compressive strength in grams per square centimeter is plotted as a function of moisture content in Figure 9 and the permeability in Figure 10.

TABLE 3.—THE PROPERTIES OF THE NATURAL BASE-SAND.

Percentage H ₂ O	Breaking Strength in Compression			Permeability
	2/3 Gms. per Sq. In.	Lbs. per Sq. In.	Gms. per Sq. Cm.	
3.85	327	1.081	75.5	35.6
8.25	424	1.402	97.9	36.2
9.70	478	1.581	110.5	35.2
12.09	489	1.617	113.0	34.2

4. SYNTHESIS OF MOLDING SAND

In order to duplicate the properties of the natural base-material from the base-sand it is necessary to restore in all essentials the original surface conditions to the base sand. This was accomplished by adding to the base-sand a synthetic iron hydrosol in place of the natural colloid removed, thereby forming a synthetic base-material.

For the duplication of the properties of the natural molding sand from the natural or synthetic base-material it is necessary to restore the bond material in all essentials. This was accomplished by adding to the natural base-material and to the synthetic base-material, synthetic bond materials. In preparing the synthetic base-material and the synthetic molding sand, silica, kaolin and an iron hydrosol were used.

Preparation of Silica.—Two hundred pounds of pure fused silica ground to pass 100 mesh was procured from the Thermal Syndicate Ltd. of Brooklyn, N. Y. The principal impurity of this material was finely divided particles of iron, just enough so that when the silica was treated with dilute acid, a trace of iron was found by the sulphocyanate test.

A slight alkalinity was also noted in the first portions of wash water from the silica.

About 100 pounds of silica was washed by decantation with water from the still, until the washings showed no trace of their original alkalinity. Incidentally this treatment removed most of the finely divided iron and some dust. The silica was thrown onto a large Buchner funnel, where a large portion of the water was removed by suction. It was placed on a large block tin tray, air dried then dried at 110° C.

After drying the silica was thoroughly mixed and three samples of 2,000 grams each sealed in glass jars. The remainder of the silica was kept in a clean paper lined burlap sack from which it was drawn as needed. A portion of this sand was sifted through a 270-mesh sieve to provide fused silica for the synthetic "bond-material" No. 1.

Preparation of Kaolin.—A quantity of Merck's kaolin and also ten pounds of a non-plastic kaolin furnished by the research laboratory of the Norton Co. through the courtesy of Messrs. Kilpatrick and Beecher of that organization were washed by decantation with pure distilled water, dried at 105-110° C. and pulverized to pass 270 mesh.

Preparation of Iron Hydrosol.—The iron hydrosol or suspension of hydrated iron oxide was prepared by a method similar to that of Neidle and Barat.²⁸ Ninety grams of C.P. $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ was dissolved in 400 cc. H_2O . To this was added dropwise with constant stirring 150 cc. of ammonium hydroxide solution made by diluting 35 cc. 0.9 sp. gr. NH_4OH to 150 cc. The solution was allowed to stand for twenty-four hours, filtered through paper on a Buchner funnel, diluted to two liters,

²⁸ *J. Am. Chem. Soc.*, 39, 79 (1917).

and dialyzed cold in a collodion bag for twenty-four hours. The dialysis was continued at 70°-90° C. The collodion bags were changed each day for the first week and every other day thereafter until the dialysis was completed. This point was considered to be reached when 500 cc. of the solution from the interior of the collodion bags evaporated to 50 cc. showed no test for iron by the sulfocyanate method or chlorine by

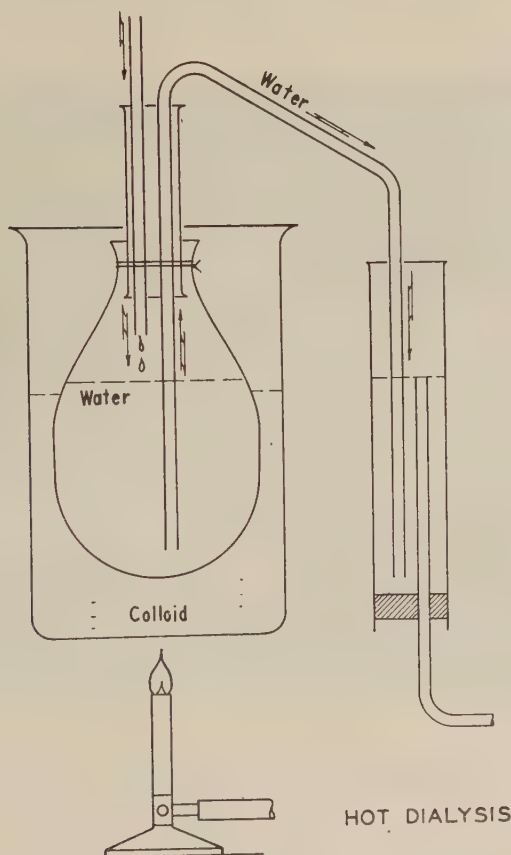
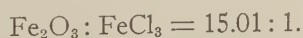


FIG. 11.

the usual procedure with silver nitrate. The analysis of the hydrosol, using the method of Thomas for chlorine and a gravimetric method for iron as iron oxide, gave the following result:



The general scheme of the dialyzing operation is shown in Figure 11. Two batteries of three dialyzing units in parallel (Figure 12) were each

fed from a five-gallon water bottle. The rate of feed during sixteen hours a day was about $1\frac{1}{2}$ to 2 liters per hour, for the remaining eight hours approximately half of that rate. The outer containers were Vollrath enameled steel pans holding about six liters. Other than a slight stain on the enamel these pans showed no marked deterioration after one month's continuous use for this purpose. At the beginning of the operation ordinary distilled water was used. The dialysis was completed with pure water from the continuous still described above. The dialyzed

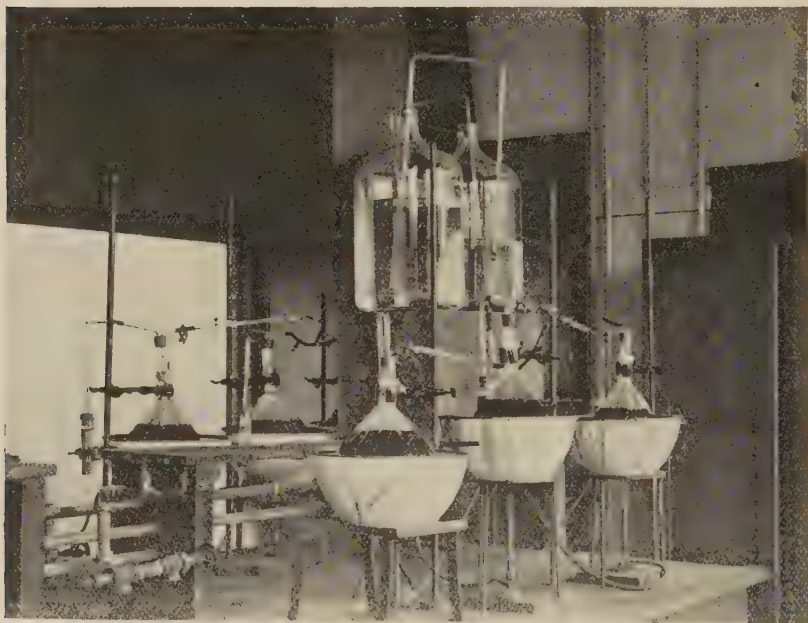


FIG. 12.

iron hydrosol was stored in glass bottles kept in a cupboard away from light.

Adsorption of the Iron Hydrosol.—The sand or clay particles were first wetted with water then mixed with the proper quantity of the iron hydrosol. The mixture of sand and hydrosol, or clay and hydrosol, was evaporated to dryness at or about 100° in a water bath, and in the case of the clay broken up so as to go through a 270 mesh sieve. For the sand sufficient hydrosol was used to give an Fe_2O_3 content of 1 per cent; for the clay the Fe_2O_3 was 0.44 per cent.

In preparing the synthetic bonds and sands the kaolin and sand, prepared separately as first described, were weighed out with an excess of water, mixed thoroughly and the excess water evaporated. The ma-

terial was air dried, then dried at 105° for one hour. This dry synthetic mixture was put through a sieve, one size larger than the largest grain of sand in the mixture, four times. The dry material was further mixed by spreading on a block tin platter and stirring systematically with a tin spoon, after which the synthetic molding sand was used directly in making up sand samples for testing.

Synthetic Bond Materials No. 1 and No. 2.—A chemical analysis of the clay-like bond material washed out of the molding sand was made. It will be noted that the water of composition of the kaolin is deducted from the total loss on ignition in the rationalized analysis.²⁹

ANALYSIS OF NATURAL BOND MATERIAL.

Chemical Analysis		Rationalized Analysis	
	Per cent		Per cent
Al ₂ O ₃	6.20	Kaolin	15.4
Fe ₂ O ₃	2.60	Fe ₂ O ₃	2.6
SiO ₂	86.10	SiO ₂	78.86
Loss on ignition.....	3.6	Loss on ignition.....	1.6
CaO	.11	CaO	.11

From this analysis, assuming that all the alumina was in the form of kaolin and that both kaolin and silica grains were coated with hydrated iron oxide, a similar synthetic bonding material was made up of the proper amounts of fused silica and kaolin ground to pass 270 mesh and carrying adsorbed ferric hydrate. This material, referred to hereafter as synthetic bond No. 1 was air dried then dried at 105° for one hour and preserved in stoppered bottles until used.

Another bond material in which the fused silica passing 270 mesh was replaced by natural base-sand of the same size obtained from the original Albany molding sand was prepared. These grains were also coated with a film of hydrated iron oxide. The synthetic bond material so obtained will be referred to hereafter as synthetic bond No. 2. It was air dried, then dried at 105° for one hour, and preserved in stoppered bottles until used.

Base-Material No. 1.—The synthetic base-material No. 1 was made by adding to ground, fused silica of approximately the same screen analysis as the natural base material, in the manner described 1 per cent of hydrated iron oxide.

The synthetic base-material No. 2 was tested for bond and permeability by the methods described with the results given in Table 4. The compressive strength in grams per square centimeter is plotted as a function of moisture content in Figure 9, and the permeability in Figure 10.

Synthetic Base-Material No. 2.—The synthetic base-material No. 2 was made by adding to the natural base-sand in the manner described 1 per cent of hydrated iron oxide.

²⁹ Mellor, *Trans. Eng. Ceram. Soc.*, **13** (1913-14); Samoylov, *Bulletin de l'Academie Imperial des Sciences de St. Petersburg*, **VI**, Ser. 31 (1909).

TABLE 4.—PROPERTIES OF SYNTHETIC BASE MATERIAL No. 1.

Percentage H ₂ O	Breaking Strength in 2/3 Gms. per Sq. In.	Compression Lbs. per Sq. In.	Gms. per Sq. Cm.	Permeability
3.97	684	2.16	158.0	22.2
6.09	787	2.60	183.5	24.2
7.93	822	2.72	191.5	24.6
10.04	838	2.77	195.0	25.0
11.93	885	2.92	206.0	25.7

The synthetic base-material No. 2 was tested for bond and permeability by the methods described and with the results given in Table 5. The compressive strength in grams per square centimeter is plotted as a function of moisture content in Figure 9, and the permeability in Figure 10.

TABLE 5.—PROPERTIES OF NATURAL BASE-SAND PLUS 1 PER CENT HYDRATED IRON OXIDE, SYNTHETIC BASE-MATERIAL No. 2.

Percentage H ₂ O	Breaking Strength in 2/3 Gms. per Sq. In.	Compression Lbs. per Sq. In.	Gms. per Sq. Cm.	Permeability
3.85	385	1.274	88.9	33.4
8.2	540	1.786	125.6	34.2
10.31	560	1.852	129.4	32.0
11.93	570	1.885	131.7	31.5

Synthetic Molding Sands Nos. 1, 2, 3.—The synthesis of a molding sand having properties similar to those of the natural sand was accomplished in three independent ways. To natural base-material thirteen per cent of synthetic bond No. 1 was added. To the synthetic base material No. 2 thirteen per cent of synthetic bond material No. 1 was added. To the synthetic base-material No. 2 thirteen per cent of synthetic bond No. 2 was added.

The first synthetic molding sand No. 1, was tested for bond and permeability by the methods described and with the results given in Table 6. The compressive strength in grams per square centimeter is plotted as a function of moisture content in Figure 9 and the permeability in Figure 10.

The second, synthetic molding sand No. 2, was tested for bond and permeability by the methods described and with the results given in Table 7. The compressive strength in grams per square centimeter is plotted as a function of moisture content in Figure 9 and the permeability in Figure 10.

The third, synthetic molding sand No. 3, was tested for bond and permeability by the methods described and with the results given in Table 8. The compressive strength in grams per square centimeter is plotted as a function of moisture content in Figure 9 and the permeability in Figure 10.

TABLE 6.—PROPERTIES OF SYNTHETIC MOLDING SAND No. 1.

Percentage H ₂ O	Breaking Strength in 2/3 Gms. per Sq. In.	Compression Lbs. per Sq. In.	Gms. per Sq. Cm.	Permeability
3.65	540	1.786	124.7	28.1
5.67	594	1.965	137.2	29.2
8.15	633	2.095	146.2	30.8
10.8	634	2.097	146.4	30.0
12.2	633	2.095	146.2	28.0

TABLE 7.—PROPERTIES OF SYNTHETIC MOLDING SAND No. 2.

Percentage H ₂ O	Breaking Strength in 2/3 Gms. per Sq. In.	Compression Lbs. per Sq. In.	Gms. per Sq. Cm.	Permeability
4.06	578	1.912	126.1	28.2
8.11	646	2.138	150.0	29.2
10.33	656	2.190	152.5	28.6
12.17	642	2.123	149.0	28.2

TABLE 8.—PROPERTIES OF SYNTHETIC MOLDING SAND No. 3.

Percentage H ₂ O	Breaking Strength in 2/3 Gms. per Sq. In.	Compression Lbs. per Sq. In.	Gms. per Sq. Cm.	Permeability
3.98	546	1.806	126.1	28.2
8.37	631	2.077	146.7	29.2
10.08	653	2.17	151.8	28.6
12.4	641	2.12	149.1	28.2

Discussion.—The graphs in Figure 9 show that the presence of the natural film of adsorbed material has a measurable effect on the strength of the base-sand. The absence of the bond material or "clay substance" causes a marked decrease in the strength of the natural molding sand. The graphs also indicate that the synthetic base-material No. 2 made from the natural base-sand and iron hydrosol is slightly stronger than the natural base-material; however, the agreement is good.

The general concurrence of the data on the strength of the synthetic molding sands as compared with that of the natural molding sands is good, and indicates that the physical strength of the natural molding sand has been substantially duplicated by that of the synthetic molding sands.

The graphs in Figure 10 show that the presence of the adsorbed film on the sand grains gives a slightly higher permeability than the sand alone. This fact and that the permeability of the natural molding sand rises to a maximum with increasing water content can be explained as due to swelling of colloidal particles and to the agglomeration of the sand grains with the bond material, thus causing larger envelopes of grain particles, with consequent lowering of resistance to air flow. When the pore space actually begins to decrease due to the filling up of the pore spaces with water the permeability to gases decreases.

The agreement of the values of permeability of the different synthetic sands is satisfactory. The permeability of the synthetic sands is more nearly constant with varying water content, which in foundry work is to be desired.

An interesting sidelight is had on the influence of grain shape by observing the behavior of base-material No. 1 made up of ground fused silica of the same screen analysis as the natural base-material. In this instance the only variable is the shape of the grain. The angular grains of the crushed silica have a higher strength and lower permeability than the more rounded grains of the natural base-sand which has a lower strength and higher permeability. This function of grain shape and permeability was first recognized and accounted for by King and Schlichter.³⁰ Angular grains when packed together have, in general, more pore space and are less permeable.

5. THE EFFECT OF HEAT ON NATURAL AND SYNTHETIC MOLDING SANDS

The behavior of molding sands when heated has been studied by a number of investigators. The experience of Dietert³¹ and Littlefield² indicates that the loss of bond observed on heating a natural molding sand to 600° F. for two hours gives a good indication of its utility as a molding sand. It is interesting to note in this connection that von Weiman and Hagiwara³² have shown that Goethite, natural crystalline ferric hydrate ($\text{Fe}_2\text{O}_3 \cdot \text{H}_2\text{O}$), loses most of its water when treated at 608° F. (320° C.). However hydrated iron oxide³³ appears to be the only metallic hydroxide that will adsorb water and regain its initial surface condition after being dried or heated to 315° C. (600° F.) or above.

For the purpose of indicating the relative durability of the synthetic and natural molding sands, the samples were heated at 600° F. for three hours, then moistened and tested in the manner described. This treatment is more severe than that recommended by Dietert³⁴ and Littlefield² in that heating was continued for three hours instead of two.

The heating of the sand was done in an ordinary Freas thermostatic oven provided with a large capacity heating coil and a heavy-duty thermo-regulator. The temperature was recorded on a calibrated Tycos nitrogen filled mercury thermometer the bulb of which was thrust into the sand being heated, care being taken that the thermometer bulb did not touch the metal pan. As the thickness of the sand layer in the pan

³⁰ U. S. Geol. Survey, 19th Annual Report (1899).

³¹ Trans. Am. Foundrymen's Assoc., 32, 24-52 (1924).

³² "Colloid Chemistry," edited by Jerome Alexander, Vol. I, p. 653. Chem. Cat. Co., New York, 1926.

³³ Paneth and Vorwerk, Z. physik. Chem., 101, 445 (1922); Hahn and Muller, Z. Elektrochem., 29, 189 (1923); Hahn, Naturwissenschaften, 12, 1140 (1924); Liebig's Ann., 440, 121 (1924).

³⁴ Trans. Am. Foundrymen's Assoc., 32, 24-52 (1924).

did not exceed one-half inch a small part of the thermometer bulb was exposed to the heated air of the thermostat. The temperature of the thermostat was held constant to $\pm 2^\circ$ F.

The dry samples of sand were spread in layers one-half inch thick in a black iron baking pan, placed in the oven, and allowed to come to a temperature of 600° F. at which temperature the material was held for three hours.

Properties of Natural Molding Sand, Heated.—The natural Albany molding sand heated at 600° F. for three hours was tested for bond and permeability by the methods described with the results given in Table 9. The compressive strength plotted as a function of the mois-

TABLE 9.—PROPERTIES OF NATURAL ALBANY MOLDING SAND HEATED TO 600° F. FOR THREE HOURS.

Percentage H ₂ O	Breaking Strength in 2/3 Gms. per Sq. In.	Compression Lbs. per Sq. In.	Gms. per Sq. Cm.	Permeability
3.6	467	1.545	108.6	35.9
6.46	547	1.760	127.2	37.8
8.11	597	1.975	138.8	33.1
9.82	609	2.013	141.6	32.4
12.32	602	1.99	140.0	30.1

ture content is shown in Figure 9 with that of the untreated sand for comparison. The permeability plotted as a function of moisture content is shown in Figure 10.

Properties of Synthetic Molding Sands Nos. 1, 2, and 3.—Synthetic molding sands Nos. 1, 2, and 3 heated to 600° F. for three hours were tested for bond and permeability by the methods described

TABLE 10.—PROPERTIES OF SYNTHETIC MOLDING SAND NO. 1 (NATURAL BASE MATERIAL PLUS SYNTHETIC BOND NO. 1, HEATED).

Percentage H ₂ O	Breaking Strength in 2/3 Gms. per Sq. In.	Compression Lbs. per Sq. In.	Gms. per Sq. Cm.	Permeability
3.92	476	1.57	110.8	33.2
5.95	558	1.84	129.8	33.0
8.2	610	2.01	141.9	34.1
9.9	613	2.02	142.6	31.3
12.1	630	2.08	146.5	30.6

TABLE 11.—PROPERTIES OF SYNTHETIC MOLDING SAND NO. 2 (SYNTHETIC BASE MATERIAL NO. 2 PLUS SYNTHETIC BOND MATERIAL NO. 1), HEATED.

Percentage H ₂ O	Breaking Strength in 2/3 Gms. per Sq. In.	Compression Lbs. per Sq. In.	Gms. per Sq. Cm.	Permeability
3.95	491	1.62	114.2	32.4
7.40	614	2.03	142.8	32.9
9.65	621	2.068	144.3	29.8
12.16	629	2.08	146.3	29.6

with the results given in Tables 10, 11 and 12. The compressive strengths are plotted as a function of the moisture content in Figure 9 and the permeabilities in Figure 10.

TABLE 12.—PROPERTIES OF SYNTHETIC MOLDING SAND No. 3 (SYNTHETIC BASE MATERIAL No. 2 PLUS SYNTHETIC BOND MATERIAL No. 2), HEATED.

Percentage H ₂ O	Breaking 2/3 Gms. per Sq. In.	Strength in Lbs. per Sq. In.	Compression Gms. per Sq. Cm.	Permeability
4.02	458	1.51	106.4	34.2
8.16	608	2.01	141.4	34.8
10.31	602	1.99	140.0	30.9
12.63	598	1.97	139.0	28.9

Discussion.—The strength of the natural and synthetic molding sands are decreased to almost the same degree by heating to 600° F. for three hours. This affords further evidence that the natural molding sand has been substantially duplicated by synthetic means.

The permeabilities of the natural and synthetic sands are increased to about the same degree by the heat treatment.

The data presented indicate that the bond, permeability, and durability of high grade natural molding sand can be substantially duplicated by synthetic means using adsorbed ferric hydrogel as a bonding agent.

6. BONDED SYSTEMS FROM PURE INGREDIENTS

The numerous constituents of natural molding sand identified by Condit³⁵ are not essential to the properties of molding sand. It has just been shown that the properties of a high grade molding sand may be duplicated by the use of only three materials, sand, kaolin and ferric hydrosol. For scientific reasons, at least, it is desirable that bonded systems of pure silica, kaolin and ferric hydrosol be investigated as well as the ordinary molding sand. The material used for this purpose were the ground fused silica, the kaolin and the ferric hydrosol already described.

The Bond Material.—The bond material used in the case of the pure materials was kaolin and kaolin treated with 0.44 per cent iron oxide as hydrated iron oxide. The kaolin untreated with the hydrosol was used to determine the effect of the absence of hydrated iron oxide. Fifteen per cent by weight of kaolin or kaolin plus 0.44 per cent iron oxide was used as the bond material in this work with pure materials.

Base Silica.—In the synthesis of the molding sand previously described the base sand furnished the starting point. In this case, the ground fused silica was used.

The base silica was tested for bond and permeability by the methods described and with the results given in Table 13. The compressive

³⁵ *Trans. Am. Foundrymen's Assoc.*, 21, 19-52 (1912).

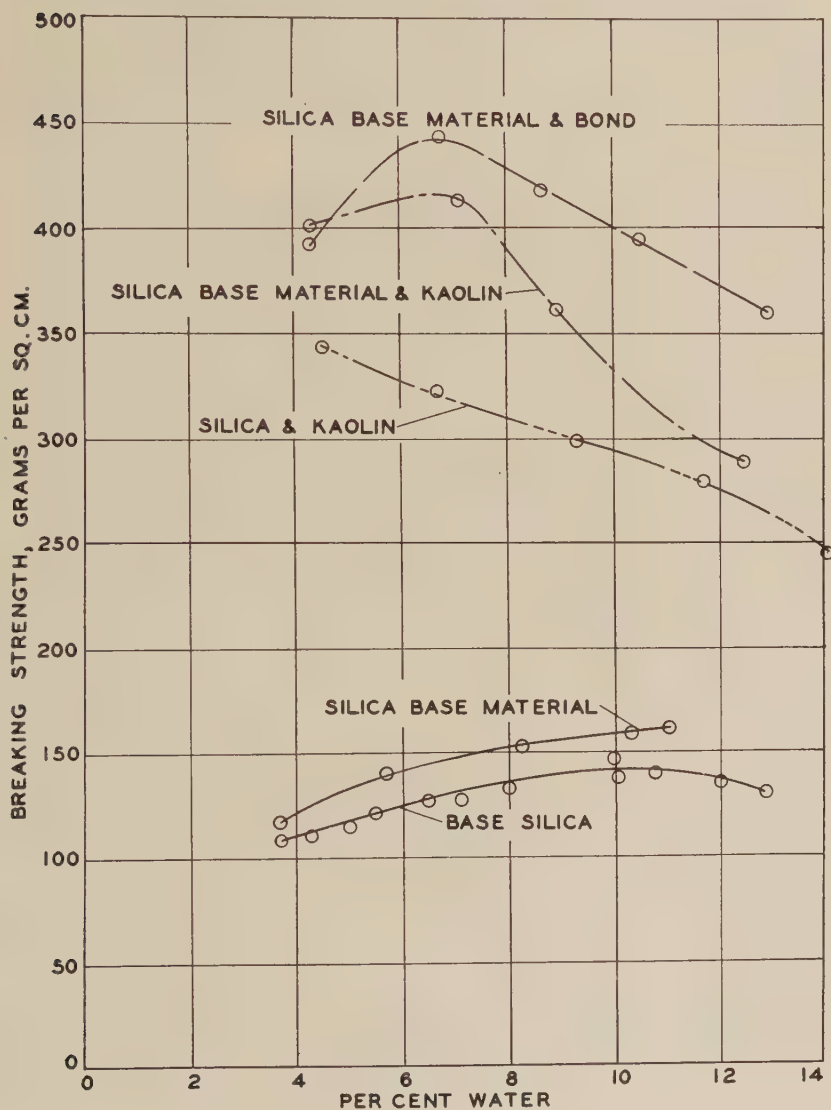


FIG. 13.

strength as a function of moisture content for the three samples is plotted in Figure 13 and the permeability in Figure 14.

Silica Base Material.—The synthesis of the silica base material was accomplished by the same method used in the preparation of the base material of the synthetic molding sand, using the base silica and

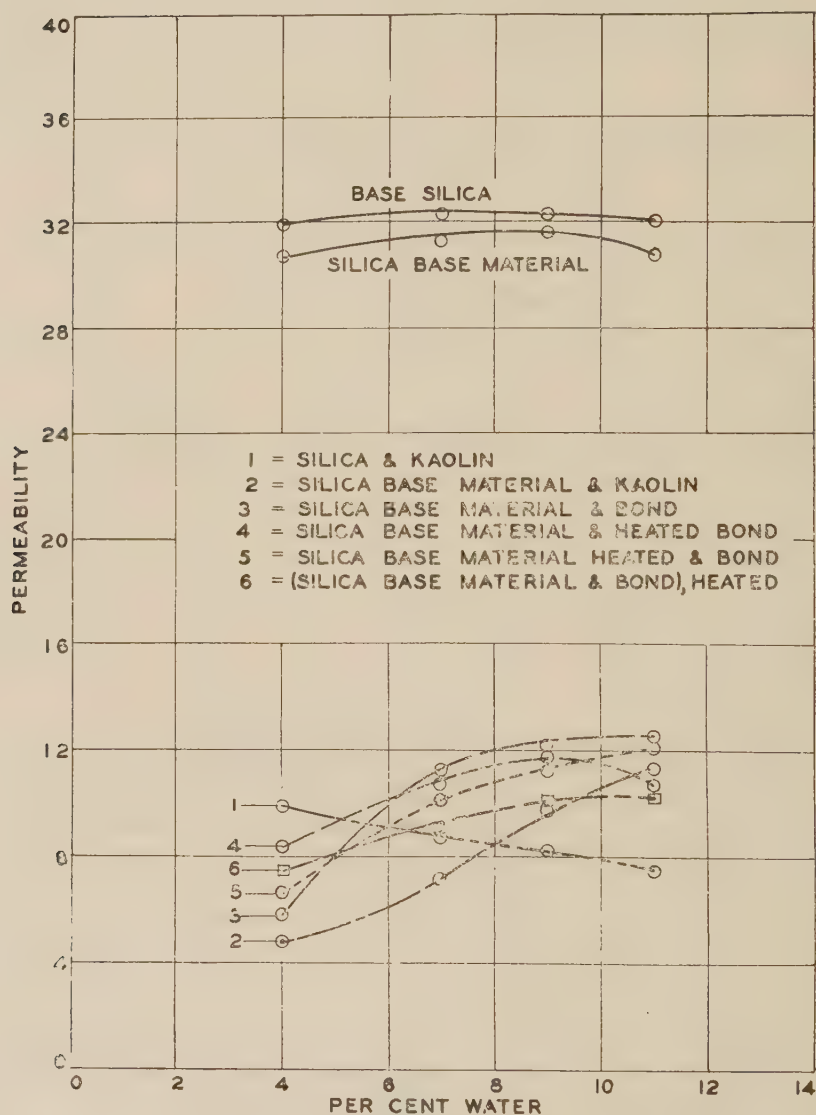


FIG. 14.

ferric hydrosol. One per cent of ferric oxide as hydrosol was added to the silica.

The silica base-material was tested for bond and permeability by the methods described. The results are plotted in Figures 13 and 20 as well as Table 14.

TABLE 13.—PROPERTIES OF BASE SILICA.

Percent- age H ₂ O	Breaking 2/3 Gms. per Sq. In.	Strength in Lbs. per Sq. In.	Compression Gms. per Sq. Cm.	Percent- age H ₂ O	Perme- ability
3.69	466	1.541	108.6	..	...
4.32	480	1.587	110.9	4	32.0
5.01	497	1.644	115.6	..	...
5.5	524	1.733	121.1	..	...
6.48	546	1.806	126.2	7	32.4
7.17	547	1.81	127.2	..	...
8.0	575	1.902	132.9	..	...
10.06	634	2.098	146.5	..	...
10.1	597	1.975	138.0	9	32.4
10.82	602	1.991	140.0	..	...
12.0	594	1.965	135.9	..	...
12.9	570	1.885	131.7	11	32.1

TABLE 14.—PROPERTIES OF SILICA BASE-MATERIAL (BASE SILICA PLUS 1 PER CENT HYDRATED IRON OXIDE).

Percent- age H ₂ O	Breaking 2/3 Gms. per Sq. In.	Strength in Lbs. per Sq. In.	Compression Gms. per Sq. Cm.	Percent- age H ₂ O	Perme- ability
3.66	498	1.647	115.7	4	30.8
5.74	602	1.99	140.0	7	31.4
8.32	656	2.17	152.5	9	31.7
10.35	686	2.27	159.5	11	30.8
11.05	690	2.28	161.0	..	...

Mixture of Silica and Kaolin.—A mixture of 85 per cent ground fused silica and 15 per cent kaolin was prepared in the manner described.

The mixture of silica and kaolin was tested for bond and permeability by the methods described with the results given in Table 15 and plotted in Figures 13 and 14.

TABLE 15.—PROPERTIES OF SILICA-KAOLIN MIXTURE.

Percent- age H ₂ O	Breaking 2/3 Gms. per Sq. In.	Strength in Lbs. per Sq. In.	Compression Gms. per Sq. Cm.	Percent- age H ₂ O	Perme- ability
4.53	1482	4.90	344.3	4	9.9
6.66	1337	4.42	322.0	7	8.8
9.33	1288	4.26	299.3	9	8.4
11.76	1207	3.99	280.8	11	7.6
14.14	1064	3.518	245.0	..	...

Silica Base Material plus 15 Per cent Kaolin.—The combination of the silica base-material and 15 per cent kaolin was brought about in the same manner and tested with the results given in Table 16 and plotted in Figures 13 and 14.

TABLE 16.—PROPERTIES OF SILICA BASE MATERIAL PLUS 15 PER CENT KAOLIN.

Percent- age H ₂ O	Breaking 2/3 Gms. per Sq. In.	Strength in Lbs. per Sq. In.	Compression Gms. per Sq. Cm.	Percent- age H ₂ O	Perme- ability
4.28	1728	5.71	401.5	4	4.8
7.05	1783	5.895	414.5	7	7.2
8.96	1555	5.14	361.5	9	9.9
12.46	1243	4.11	289.0	11	11.4

Silica Base Material plus 15 Per cent "Bond Material" (Kaolin with 0.44 Per cent Iron Oxide as Hydrated Iron Oxide).—To the silica base-material 15 per cent of kaolin containing 0.44 per cent of iron oxide was added in the manner described.

The combination of silica base material with kaolin carrying 0.44 per cent iron oxide as hydrated iron oxide was tested for bond and permeability by the methods described and with the results given in Table 17 and plotted in Figures 13 and 14.

TABLE 17.—PROPERTIES OF SILICA BASE MATERIAL PLUS 15 PER CENT KAOLIN CONTAINING 0.44 PER CENT IRON OXIDE AS HYDRATED IRON OXIDE.

Percent- age H ₂ O	Breaking Strength in 2/3 Gms. per Sq. In.	Strength in Compression Lbs. per Sq. In.	Gms. per Sq. Cm.	Percent- age H ₂ O	Perme- ability
4.23	1688	5.58	392.2	4	5.8
6.72	1911	6.32	444.0	7	11.3
8.65	1804	5.96	418.2	9	12.3
10.50	1700	5.62	395.0	11	12.6
12.93	1548	5.115	360.0	..	...

Discussion.—The presence of the surface film of hydrated iron oxide on the fused silica base causes an increase in the strength of the material similar in character to that observed when the natural base-sand was treated with the iron hydrosol.

The presence of the hydrated iron oxide film on the silica is shown to exert a marked influence on the strength of silica-kaolin mixtures. Hydrated iron oxide films on both silica and kaolin give a further increase in strength, especially at the higher water contents.

The permeability of the silica-kaolin mixtures decreases with successive additions of water while the permeability of the silica-kaolin-iron oxide combinations shows an increase with water content. This may be taken as an indication that adsorbed hydrated iron oxide on the particles of silica is present as a gel which takes up water and swells thereby forming larger particles tending to become spherical or causing the separate grains to agglomerate, in either case increasing the permeability of the mass.

7. THE CAUSE OF THE DECREASE IN BOND ON HEATING

The effect of heating the silica-kaolin-iron hydrogel system was investigated to determine the probable cause of the decrease in bond on heating. For this purpose the silica base material and the bond material were heated separately, then mixed with unheated bond and base material respectively, and compared with the mixture of unheated material and the bonded system mixed before heating.

The kaolin bond material containing the adsorbed hydrated iron oxide was heated at 600° F. for three hours, cooled to room tempera-

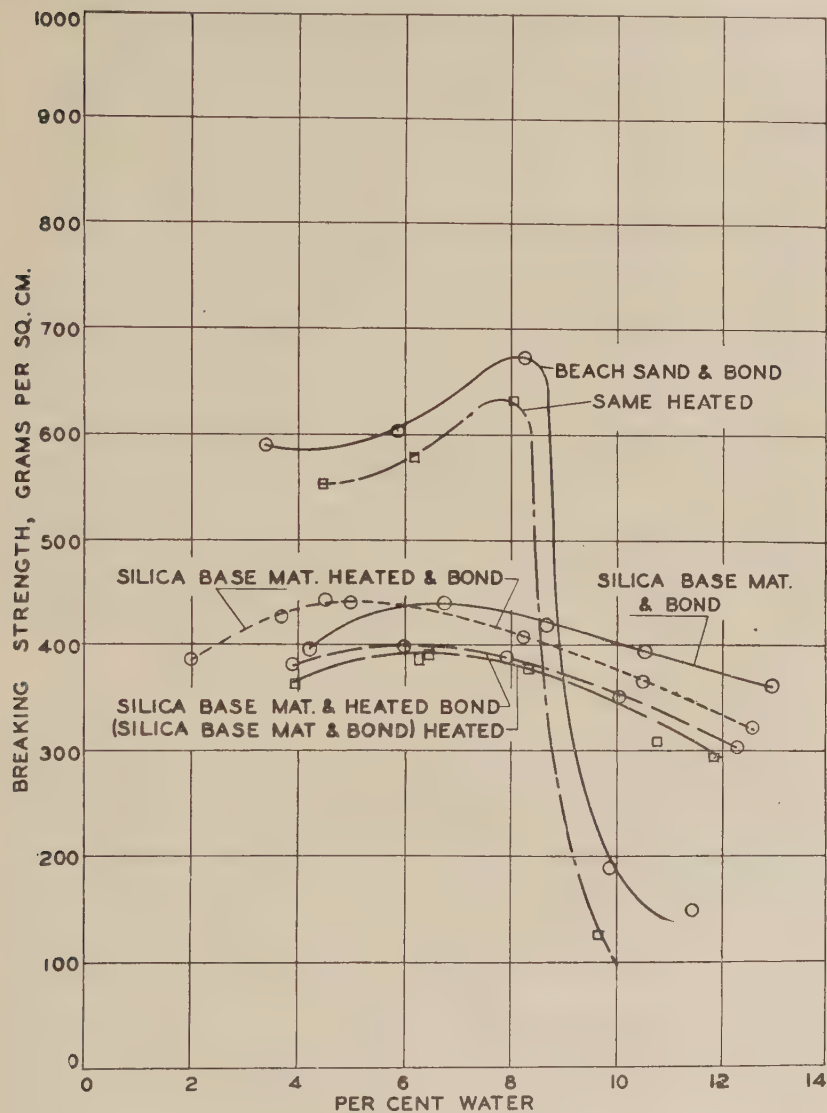


FIG. 15.

ture, and mixed with the silica base material in the manner described. This mixture was tested for bond and permeability with the results given in Table 18 and plotted in Figures 14 and 15.

The silica base material was heated at 600° F. for three hours, cooled to room temperature, and combined with the kaolin bond mate-

TABLE 18.—PROPERTIES OF THE SILICA BASE-MATERIAL PLUS (KAOLIN CONTAINING 0.44 PER CENT IRON OXIDE AS HYDRATED IRON OXIDE, HEATED TO 600° F. FOR THREE HOURS).

Percent- age H ₂ O	Breaking Strength in 2/3 Gms. per Sq. In.	Strength in Lbs. per Sq. In.	Compression Gms. per Sq. Cm.	Percent- age H ₂ O	Perme- ability
3.9	1650	5.455	383.5	4	8.4
6.0	1720	5.685	400.0	7	10.8
7.95	1680	5.528	390.5	9	11.85
10.1	1515	5.02	352.0	11	10.8
12.3	1307	4.32	304.0	..	...

rial in the manner described. This mixture was tested for bond and permeability with the results given in Table 19 and plotted in Figures 14 and 15.

TABLE 19.—PROPERTIES OF SILICA BASE MATERIAL HEATED AT 600° F. FOR THREE HOURS PLUS 15 PER CENT KAOLIN CONTAINING 0.44 PER CENT IRON OXIDE AS HYDRATED IRON OXIDE.

Percent- age H ₂ O	Breaking Strength in 2/3 Gms. per Sq. In.	Strength in Lbs. per Sq. In.	Compression Gms. per Sq. Cm.	Percent- age H ₂ O	Perme- ability
2.0	1673	5.515	389.0	4	6.7
3.7	1850	6.116	430.0	7	10.2
4.55	1918	6.34	446.0	9	11.3
5.0	1898	6.274	441.0	11	12.1
8.25	1741	5.76	409.5	..	...
10.55	1576	5.21	366.2	..	...
12.6	1393	4.60	322.9	..	...

The silica base-material was mixed with the bond material (kaolin with 0.44% iron oxide as hydrated iron oxide) and the mixture heated at 600° F. for three hours. This heated mixture was tested for bond and permeability with the results given in Table 20 and plotted in Figures 14 and 15.

TABLE 20.—PROPERTIES OF SILICA BASE MATERIAL PLUS 15 PER CENT KAOLIN CONTAINING 0.44 PER CENT HYDRATED IRON OXIDE, HEATED AT 600° F. FOR THREE HOURS AFTER MIXING.

Percent- age H ₂ O	Breaking Strength in 2/3 Gms. per Sq. In.	Strength in Lbs. per Sq. In.	Compression Gms. per Sq. Cm.	Percent- age H ₂ O	Perme- ability
3.96	1575	5.204	366.0	..	...
6.28	1670	5.51	388.0	4	7.5
6.42	1695	5.60	394.0	7	9.1
8.4	1635	5.40	380.0	9	10.0
10.8	1333	4.405	310.0	11	10.4
11.86	1296	4.222	295.0	..	...

Discussion.—Heating the silica base before mixing it with the bond material has no noticeable effect on the maximum strength of the bonded system. This indicates that the loss in bond on heating, at least to 600°

F. for 3 hours, is not due to any change in the ferric hydrogel adsorbed on the silica. This fact is a further verification of that reported by Hahn³³ that hydrated ferric oxide is reversibly peptized on heating. Heating the silica base does seem to shift the point of maximum bond toward drier mixtures from about 7 to 5 per cent water content. This may be due to the heated gel being more easily wetted and therefore weaker at the higher water contents.

On the other hand, heating the bond material before mixing with on the silica. This fact is a further verification of that reported by lost on heating. This clearly indicates that the loss in bond on heating is due entirely to changes in clay bond. Although the mineral kaolinite ($\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2 \cdot 2\text{H}_2\text{O}$) has shown no evidences of decomposition at temperatures as low as 600° F.³⁶ other hydrous aluminum silicates probably present in kaolin such as Halloysite and Allophane³⁷ show evidences of dehydration at temperatures as low as 300° F. (150° C.). Bigot reports that clays are partially irreversibly pektized at 350° to 600°.

With these facts in mind it seems evident that the loss in strength on heating is due to changes in the clay, either by decomposition of the crystal structure or by changes in surface conditions, and not due to changes in the sand particles or in the ferric hydrogel.

HIGH GRADE MOLDING SAND FROM UNBONDED BEACH SAND

The results of this work clearly indicate the possibility of preparing high grade synthetic molding sands to meet specifications for certain uses. As a demonstration a clean beach sand from the Michigan City district was mixed; treated with iron hydrosol and mixed with 15 per cent kaolin containing 0.44 per cent hydrated iron oxide as described. This synthetic material was tested for bond and permeability by the methods described with the results given in Table 21 and plotted in Figure 15.

TABLE 21.—PROPERTIES OF MICHIGAN CITY SAND BASE MATERIAL PLUS 15 PER CENT KAOLIN CONTAINING 0.44 PER CENT HYDRATED IRON OXIDE.

Percentage H ₂ O	Breaking Strength in		Compression Gms. per Sq. Cm.	Permeability
	2/3 Gms. per Sq. In.	Lbs. per Sq. In.		
3.41	2525	8.44	592.0	...
5.90	2600	8.6	604.0	...
8.32	2910	9.63	676.0	45
9.89	813	2.69	189.0	...
11.44	641	2.12	149.0	...

³⁶ S. Satoh, *J. Am. Cer. Soc.*, 4, 182 (1921).

³⁷ Le Chatelier, *Compt. rend.*, 104, 1443 (1887); Ding. polyt. J., 265, 94 (1887); A. Bigot, *Compt. rend.*, 176, 91 (1923).

The same sample was dried and heated at 600° F. for three hours, then tested for bond and permeability, with the results given in Table 22 and plotted in Figure 15.

TABLE 22.—PROPERTIES OF MICHIGAN CITY BASE MATERIAL PLUS 15 PERCENT KAOLIN CONTAINING 0.44 PER CENT HYDRATED IRON OXIDE HEATED TO 600° F. FOR THREE HOURS.

Percentage H ₂ O	Breaking Strength in Compression			Permeability
	2/3 Gms. per Sq. In.	Lbs. per Sq. In.	Gms. per Sq. Cm.	
4.5	2390	7.92	556.0	...
6.2	2500	8.38	581.0	...
8.1	2720	9.02	633.0	55
9.7	540	1.79	125.5	...
12.0	wet	...		...

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